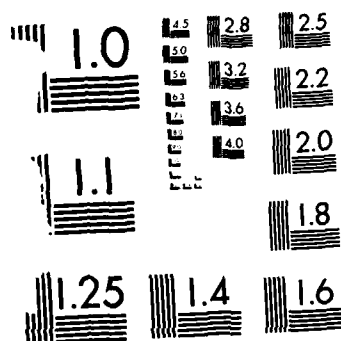|			
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OPTICAL ABSORPTION CHARACTERISTICS OF AEROSOLS

E. M. Patterson

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11 September 1985

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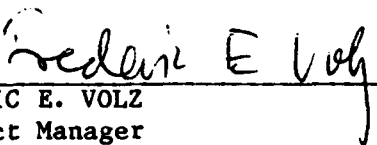26 January 1982-30 June 1985

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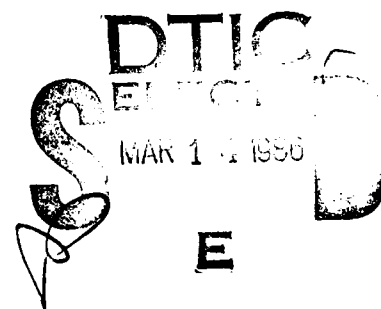
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This technical report has been reviewed and is approved for publication.

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The absorption of well documented, highly absorbing submicron aerosols has been measured by means of diffuse reflectance and diffuse transmission techniques. The intent of these measurements was to compare the different techniques and to provide calibration of these absorption measurements in terms of aqueous transmission measurements.

These measurements indicate that there is a consistency among the absorption techniques that the differences between absorption in an aqueous and in an air suspension need to be considered in calibrations of absorption techniques, and that the diffuse transmission and diffuse reflectance measurements using the dilution technique appear to yield consistent results.

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INTRODUCTION

The absorption of visible and near visible radiation by the atmospheric aerosol is often a significant component of the aerosol radiative effects. This absorption is important because of its direct effect on visibility reduction and on radiative transfer in the atmosphere (see e.g. Groblicki et al, 1984), as well as its possible effect on radiative transfer in optically thick cloud layers (Patterson et al, 1984). The possible climatic effects of the aerosol, for example, will be determined in large part by the ratio of absorption to scattering in the aerosol. In addition, the interpretation of remotely sensed data and the proper consideration of atmospheric effects on this data requires knowledge of the absorption properties as well as the scattering properties of the aerosol.

The aerosol absorption can have a very wide range of variation. Expressed as a percentage of the total light extinction by an aerosol, the absorption at visible wavelengths can range from much less than 1 % of the extinction in a white, low absorption material such as ammonium sulfate or ammonium nitrate to more than 90% of the total extinction in highly absorbing soots and smoke emissions. The wide range of the measured absorption under different ambient conditions was shown by Gerber (1981).

For highly absorbing materials, in particular, an accurate

assessment of the aerosol radiative effects requires accurate determinations of the aerosol absorption. There appear, however, to be some significant systematic differences in the results obtained using different experimental techniques. These differences were shown in a recent set of absorption measurement intercomparisons discussed by Gerber and Hindman (1981). There was a range of roughly a factor of two among the various absorption measurements for both a soot aerosol and a methylene blue aerosol measured in the intercomparison.

While these intercomparisons provided valuable insights into the limitations of the different absorption measurement methodologies, no attempt was made in that study to choose any one of the methodologies as a standard against which the others could be judged. There was also no attempt to make calibration measurements with aerosols whose absorption was determined independently of the intercomparison. And, in general, there have been relatively few calibrations for the commonly used absorption techniques using materials for which the bulk optical constants are known independently.

We have made a series of absorption measurements of laboratory aerosols that are an extension of the work presented in Gerber and Hindman. The goal of the measurements discussed here was twofold: first, to make further comparisons of several methodologies for measuring aerosol absorption and second, to go beyond a simple comparison of methods by providing a calibration for the measured

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aerosol absorption in terms of standard, well determined measurements. The experimental procedures included laboratory generation of aerosols from several different materials, measurement of aerosol absorption by two diffuse reflectance techniques and one diffuse transmission technique, and measurement of the absorption of an aqueous suspension or solution of each material. The measurements emphasized a study of an aqueous suspension of carbon black (Mars ink) as a reproducible analog of the soot which is believed to be responsible for much tropospheric absorption. As a stable suspension with well defined and documented physical properties it is well suited for our characterization measurements.

Variations in the individual techniques were investigated; in addition, absorption measurement comparisons were made for other aerosols that were not as suitable for such extended laboratory studies.

In this report, several comparisons of results of different methods of measuring absorption for a variety of materials are presented; and some of the limitations of the different methods are discussed. The measured aerosol absorption is discussed in relation to the absorption of an aqueous suspension which provides a calibration for the aerosol measurements. The Mars ink results are discussed in considerable detail.

ABSORPTION PARAMETERS

The results of aerosol absorption measurements can be reported
in terms of absorption parameters that are characteristic of the
aerosol suspension or of the bulk material making up the aerosol.
For a bulk non-scattering material the absorption may be described
in terms of the Lambert absorption coefficient k, with k defined by
the equation

$$k = - (1/x) \ln (I/I_o) \tag{1}$$

with x the path length through the absorbing material, I_o the
incident intensity, and I the intensity of the transmitted light.
The turbidity δ is a measure of the total light reduction by the
absorbing material and is given by the equation

$$\delta = - \ln(I/I_o) \tag{2}$$

δ and k, then, are related by the equation

$$k = \frac{\delta}{x} \tag{3}$$

For the usual laboratory transmission spectroscopy measure-
ments, the value of x, the path length through the sample, is not
always a readily measurable quantity. Another absorption parameter,
the specific absorption B_a, may be defined in terms of the directly

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measured δ and the ratio M/A, the mass of absorbing material M per unit area A illuminated by the spectrometer beam. As defined, a determination of B_a does not require a knowledge of the density ρ of the absorbing aerosol.

The equation for B_a can be written in terms of these directly measured quantities as

$$B_a = \frac{\delta A}{M} \tag{4}$$

B_a is then related to the Lambert absorption coefficient, k by the equation

$$B_a = \frac{k}{\rho} \tag{5}$$

Another widely used absorption parameter is the imaginary part of the complex index of refraction, n_2, which is used in Mie calculations. For a bulk non-scattering material, n_2 is related to the specific absorption by the equation

$$n_2 = \frac{B_a \rho \lambda}{4\pi} \tag{6}$$

with λ the wavelength of the incident light.

When the absorbing material consists of discrete absorbing and scattering particles imbedded in a material with a differing refractive index, the above relations must be modified to take the effects of scattering into account. The aerosol absorption may be charac-

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terized by a volume absorption coefficient σ_a, which is defined analogously to the extinction coefficient σ_e and the scattering coefficient σ_s; it is defined as the total energy removed by absorption from the incident beam per unit path length by the aerosol particles. For the aerosol suspension,

$$\sigma_a + \sigma_s = \sigma_e. \qquad (7)$$

A specific absorption may be defined for the aerosol in an analogous fashion to the definitions in Eq (4) and Eq (5) as the ratio of the *volume absorption coefficient* to the mass concentration of the aerosol, M_v, according to the equation

$$B_a = \frac{\sigma_a}{M_v}. \qquad (8)$$

The equivalence between the definitions in Eq (4) and Eq (8) may be seen by considering the mass of aerosol material in a volume that is defined by a cross sectional area A and a length x. If both the numerator and the denominator of Eq (8) are multiplied by the length x then the numerator can be written as δ_a, the turbidity due to absorption; and the denominator is the mass per unit area responsible

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for producing the δ_a. It must be remembered, of course, that the scattering is responsible for a significant portion of the extinction and that B_a is defined in terms of the absorption only. Laboratory measurements of aerosol absorption generally involve the collection of aerosol material; and the assumption is made that the absorption is not changed by the process of collection. B_a for the aerosol can then be inferred from the laboratory measurements if the effects of aerosol scatter can be accounted for in an appropriate manner.

For an aerosol, the relationship between B_a and n_2 depends in part on the real component of the refractive index, n_1, of the discrete particles relative to that of the surrounding medium; and Eq (6) must be modified. For an aerosol consisting of particles that are small relative to the wavelength of the incident light and that have n_1 values between 1.25 and 1.75 and n_2 values of less than 1, Hänel and Dlugi (1977) have used the equation

$$n_2 = \frac{B_a \ \rho \ \lambda}{4 \ \pi} \ \frac{(n_1^2 + 2)}{3} \qquad (9)$$

which is derived from an expression of Penndorf(1962) to approximate the relation between B_a and n_2.

Bohren and Huffman (1983) present a slightly different equation relating n_2 to B_a

$$n_2 = \frac{B_a \rho \lambda}{4\pi} \left[\frac{(n_1^2 + 2)^2}{9 n_1} \right] \qquad (10)$$

Both equations have the same range of validity; within their range of validity, the two equations differ by $\approx 5\%$. Both are strictly applicable only in the Rayleigh (small particle) limit; for somewhat larger particles, the relationship between n_2 and B_a is more complex and is dependent on particle size as well as refractive index value. For particles that range in size up to size parameter $x \approx 1$ (with x defined as the ratio $x = 2\pi r/\lambda$, with r the particle radius) the approximate relationship will be accurate to within about 40% compared with exact Mie calculations.

An example of the relation between the approximations of equations (9) and (10) and the exact Mie calculations, expressed in terms of the absorption efficiency Q_a is shown in Fig 1. The solid line is a plot of the absorption efficiency determined by exact Mie calculations. The dashed line is a plot of the absorption efficiency to be expected using Equation (10), assuming the given refractive index. It is apparent from the curve that the use of Equation (10) to determine a value of n_2 from the measured B_a will lead to an overestimation of n_2 for size parameters near 1. For aerosols in this size range a more accurate inference of n_2 from the B_a data can be made using the appropriate Mie calculations.

Because B_a depends on n_1 as well as on n_2, the B_a value mea-

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sured for a highly absorbing particle will depend on the value of n_1 relative to the surrounding medium. As Bohren and Huffman (1983) have discussed, the measured absorption for an aqueous suspension of small highly absorbing particles will be expected to be greater than that of an air suspension of the same particles. Comparisons between measurements of aqueous and air suspensions must take these differences into account.

EXPERIMENTAL METHODS

Materials Studied

In this study, aerosols were generated using Staedtler Mars 745 black drawing ink, Flo-Master ink, and nigrosine dye. The Mars ink consists of gas-soot (carbon black) particles with a dispersing agent in an aqueous suspension. The carbon black particles have an approximately log-normal size distribution with a mass mean diameter of about 0.09 and a σ for the distribution of 1.6 (Hogan et al, 1985). The Mars ink consists of $\approx$ 0.22 g of solid material per ml of ink; the density of the solid material in the ink is $\approx$ 1.8 g/cm^3.

The Flo-Master ink, unlike the Mars ink, consists entirely of material that is soluble in organic solvents. The nigrosine dye is a biological stain that is available from Eastman Organic chemicals. The solid nigrosine dye has a density ρ of 1.4 g/cm^3. The nigrosine dye solution is stable, with stable absorption properties. Its behavior in solution may be referenced against standard absorption

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data determined by the dye manufacturer. These materials were chosen because of their high absorption, the ease of generation of aerosols using these materials, and the ability to characterize the generated aerosol particles. Methylene Blue, the aerosol used in the earlier absorption intercomparison, was not used because our experience subsequent to the earlier study showed that this material was not stable and that its optical properties changed with time.

In addition to these laboratory aerosols, absorption measurements were made for volcanic ash aerosols and for smoke emissions from laboratory fires using diffuse transmission and diffuse reflectance techniques.

Aerosol Generation

The aerosols were generated using an atomizer system in which humidified compressed air was bubbled through a suspension (or solution) of the ink. The nigrosine dye and the Mars ink were diluted with water; for the flowmaster ink, an organic solvent was used for the dilution. The resulting aerosol was passed though an impaction system to remove the larger particles before drying. The aerosol generation system produced relatively large quantities of aerosol particles with stable size distributions.

Sizes of the generated aerosols were measured from scanning electron micrographs; size distributions were also measured using a single particle optical counter. An example of the size distribution measured for the Flo-Master ink is shown in Fig. 2. The curves

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show data determined from the micrographs as well as data determined from the optical particle counter. There is rough agreement between the curves, even though no explicit calibration for the absorbing aerosol was made. We can see from the curves that the mass of the aerosol is concentrated in the sizes between 0.1 and 1 μm. The sizes of the nigrosine particles were slightly smaller than the sizes of the Flo-Master particles shown in Fig.2. The size distributions for the Flo-Master ink and the nigrosine dye depended on the operating characteristics of the generation system and on the initial concentration of the ink. Since the Mars ink consisted of a suspension of solid particles the size distribution of the aerosol was more strongly influenced by the original size distribution of the carbon black particles. At the dilutions used in the aerosol generation system for this study, however, some of the generated particles contained more than one of the carbon black particles and there was some agglomeration on the filters.

Absorption Measurements

Absorption measurements were made using a diffuse transmission technique and two diffuse reflectance techniques; absorption measurements were also made using solution transmission techniques.

The diffuse transmission (DT) method of measuring aerosol absorption, which has been described by Patterson and Marshall (1982), is a variation of the integrating plate method described by Lin et al (1973) and the laser transmission technique of Rosen et al

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(1978). Essentially, the technique involves a measurement of the intensity of laser light that is diffusely transmitted by a loaded aerosol filter relative to that transmitted by a blank filter and the calculation of a turbidity δ from these relative intensities. The filter is backed with a plastic diffuser to produce diffusely transmitted light whose angular distribution of intensity has a cos θ dependence, where θ is the angle from the normal to the diffuser surface. With this diffuser, the angular dependence of the transmitted light is the same, whether the aerosol is present or not. The measured intensity does not depend on the details of the forward scattering by the aerosol sample, and the reduction in measured intensity is due only to the light absorbed by the sample and to that backscattered by the sample. The backscattered fraction of light, then, must be much smaller than the absorbed fraction. For most aerosols, the backscatter fraction is less than 10% of the total scattering and this requirement will be met except in cases in which the absorption is very low. This requirement is met for the highly absorbing samples considered in this study.

In this DT method, the σ_a values are determined from the turbidity δ of the filter, the area of the filter and the air flow through the filter during the sample collection. B_a values are determined from the above data and the mass of material on the filter. It has been shown that the response of these transmission methods can be dependent on filter type and orientation (Patterson and Marshall, 1982). Various studies (see for example Patterson and Mar-

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shall) have shown that the use of a Nuclepore filter with the aerosol sample oriented toward the incident laser beam will minimize any enhancement due to filter effects. This study, then, has emphasized measurements with samples collected onto Nuclepore filters.

The diffuse reflectance techniques make use of the fact that the total diffuse reflectance of a powder surface is determined by the absorption and scattering properties of the powder as well as the thickness of the layer. For a layer that is thick enough so that no light is transmitted, the Kubelka-Munk theory, which is a two stream radiative transfer model, relates the reflectance to the ratio of the absorption to the scattering. The Kubelka-Munk theory has been shown to be an accurate description of the reflectance when there is no specular component of the reflectance and when the absorption is small relative to the scattering.

Two diffuse reflectance techniques were studied. In one, the dilution method (DR), the aerosol material is mixed with a highly reflecting barium sulfate powder and the total diffuse reflectance of the mixture is measured using an integrating sphere. The reflectance of the mixture is, in general, less than the reflectance of the pure barium sulfate. The dilution is great enough so that the scattering properties of the mixture are the previously measured scattering properties of the barium sulfate, and so the decrease in reflectance due to the addition of the aerosol is attributed solely to aerosol absorption. The absorption of the aerosol can then be determined from the known concentration of the aerosol in the mix-

ture and the absorption of the mixture with the application of an appropriate mixing rule. The usual assumption is that volume average mixing rules apply. A more complete description is given in Patterson et al (1977) and Patterson and Marshall (1982).

According to the Kubelka-Munk theory, for finely divided powders, the DR technique provides a direct measure of the B_a for the bulk material; k can be determined if the density of the aerosol material is known. Under the assumptions of the Kubelka-Munk theory, the imaginary component of the refractive index is determined using Equation (6).

The other diffuse reflectance method studied is a filter reflectance (FR) method that was originally described by Lindberg and Snyder(1973). This reflectance method also uses the Kubelka-Munk formalism. In the FR method the reflectances of both a loaded Nuclepore filter and a blank filter are measured with a dark and with a white background. These four reflectance values are interpreted to determine the Kubelka-Munk scattering and absorption for the aerosol, as well as the bulk absorption k and the imaginary component of the refractive index n_2.

The solution transmission measurements used dilutions of the inks and dye in standard spectrometer cells. The absorption of the material was inferred from the measured turbidities and the known concentrations of the materials in the cells using standard procedures. It was expected that these materials should follow Beers law, with the turbidity proportional to the concentration, for low

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concentrations; for higher concentrations, deviations from such linearity allow the estimation of the effects of scattering. For low concentrations, the absorbing materials followed Beers law, as expected. In one of the cases, that of the Mars ink, deviations from linearity were used to infer a contribution of scattering to the turbidity.

The DT and the FR measurements used the aerosols generated by the generation system. The DR measurements were made using an evaporative residue for the bulk material. For dilute material in which there is a specific residual particle size such as the Mars ink, this should cause no problems. For the other inks and dyes, this difference in technique must be considered in the analysis of the comparisons.

ABSORPTION RESULTS AND COMPARISONS

Comparisons of absorption methodologies were made for the DR, the FR, and the DT techniques for the laboratory generated materials as well as for the additional materials considered. As discussed above, an emphasis was placed on the Mars ink measurements as an analog for atmospheric soot. The Mars ink carbon black suspension, the other laboratory aerosols, and the additional materials are discussed separately below.

Absorption of a Carbon Black Suspension (Mars Ink)

Several series of measurements were made using the Mars ink carbon black suspension. Aqueous transmission measurements were made using a 1.0 cm path length cell with different dilutions of the Mars ink. Turbidity values were calculated from the data; a set of these turbidity values vs mass concentration of the solid ink material is shown in Fig. 3.

Since the data are for transmission through an aqueous suspension of the particles, the extinction is due to both scattering and absorption. As a result the plot of turbidity vs mass concentration is not a straight line at the higher turbidities and there are deviations from Beers law. The deviations from Beer's law for the different ink dilutions were used to infer in an approximate way the relative importance of scattering in producing the extinction. This was done by calculating the best fit line of turbidity vs mass concentration for the low concentration data that is shown in Fig. 3 and considering that this would be the expected turbidity in the absence of multiple scattering. A radiative transfer routine was used to calculate the expected transmission for differing values of ω, the ratio of the scattering to the extinction, for expected turbidity values of 3 and 4. The inferred ω was that which best reproduced the observed transmission values. Using this procedure, we inferred an ω of 0.15, which is in general agreement with the data of Hogan (1984), who also inferred that scattering was only a small portion of the extinction of the aqueous suspension.

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Use of this value of ω, together with the extinction values inferred from the low concentration transmission data and the data on the mass concentration in the suspension, allows us to determine a value of B_a of 3.5 m^2/g at $\lambda=633$ nm for the aqueous suspension of the solid material. Following the discussion in Bohren and Huffman (1983), this measured value of B_a for the aqueous suspension will not be the B_a value expected for an aerosol suspension. If a value of 1.7 is assumed for the real component of the refractive index in air, then the aqueous data imply a B_a value of 2.6 m^2/g for the particles as an air suspension.

It should be pointed out that this difference in absorption will affect measurements such as those of Heintzenberg (1982) in which the absorption of a liquid suspension is measured. His reported value of 9.68 m^2/g for B_a for an aqueous suspension will actually correspond to a somewhat lower aerosol value.

A plot of δ determined using the diffuse transmission technique for $\lambda = 633$ nm is shown in Fig. 4. Attempts to fit the total data set to a single regression line resulted in a y-intercept value that was significantly greater than 0, indicating some inconsistencies in the data. Use of the low concentration turbidity data only did result in a y-intercept that did not differ significantly from 0 and so this low turbidity, low concentration data was used in the subsequent analysis. The filter area is 14 cm^2 and the low mass loading data imply a B_a of 2.4 m^2/g.

Measurements of B_a were made using the DR and the FR methods.

The DR method,which involved the dilution of the sample, resulted in a value of B_a of 3.0 at 633 nm. For these highly absorbing particles, however, great care had to be taken to insure that the particles were not aggregated into much larger particles for which the effective B_a would be lower than the B_a for the separate particles; for those cases in which such care was not taken, the measured values were lower than our reported values by factors of 2 to 3. The FR method, by comparison, produced results that were somewhat lower than the other measured values by approximately a factor of 2.

An overall comparison of the results from the aqueous transmission measurements, the DR measurements, and the DT measurements is shown in Fig. 5. It is apparent that there is a substantial agreement among these three methods at the 633 nm wavelength as well as at the other wavelengths measured. Since the aqueous transmission measurements provide a direct measure of the absorption, the agreement between the corrected values determined from the aqueous measurements and the DT and DR measurements indicates that there are no substantial systematic errors in these aerosol measurements. There do appear to be some systematic errors in the FR measurements. These errors may be related to the high absorption of the samples, since the Kubelka-Munk theory will not produce as accurate results for high absorption powders as for low absorption powders (Kortum, 1969).

Measured B_a values have been used to calculate n_2 values at 633 nm for each of the measurements shown in Fig. 5. n_2 for the DR

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data was calculated using Eq (6). n_2 for the two other measurements was determined from Mie calculations of absorption for the size distribution of the Mars ink using a range of n_2 values appropriate to both air and water. The n_2 value that reproduced the measured B_a values was considered to be the best value. We would add the caveat that the actual sizes on the filters are somewhat larger than indicated due to agglomeration and that the actual value of n_2 for the Mars DT data will be somewhat less than indicated.

The results of these calculations are shown in Table 1. It is apparent that there is a substantial agreement in the n_2 values as shown in the Table. The values for n_2 that would be calculated with the use of Eq (10) are also shown for comparison.

Nigrosine Dye Measurements

Nigrosine absorption was determined for an aqueous solution of the dye and for an aerosol consisting of the dry nigrosine material formed by the evaporation of the droplets produced by the aerosol generation system. Nigrosine absorption data are shown in Figs. 6 (aqueous solution data) and 7 (aerosol data). The aqueous data were determined by standard solution techniques with a 10 cm cell; the aerosol data were determined by the DT technique. These solution data were consistent with the manufacturer's specifications for absorption. Since the nigrosine dye forms an aqueous solution rather than a suspension, the effects attributed to discrete particles were not observed in the aqueous data.

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The plot of turbidity vs mass concentration for the nigrosine shows no deviations from linearity that indicate a significant contribution of scattering to the extinction; consequently no adjustments to the aqueous data to take account of scatter were made. The data imply a B_a of $3.6 m^2/g$ at 633 nm for the Nigrosine in an aqueous solution. The diffuse transmission measurements, made with the Nigrosine in solid aerosol form, imply a B_a of 3.7 m^2/g. The differences in these values represent a difference of less than 5 %. The uncertainties in each of the values of B_a are estimated to be approximately 10 to 15 %, and so the values are considered to be in excellent agreement.

Measurements made with the DR technique for the nigrosine, however, showed a B_a value of 0.9 m^2/g at 633 nm, a value significantly lower than the DT and the aqueous solution value. The reasons for these differences are not known at this time. FR measurements were not made for the nigrosine

The B_a values at 633 nm were used to calculate n_2 values for the nigrosine. The aqueous transmission data results in a value of 0.25 for n_2; by comparison, a value of n_2 of 0.20 was inferred from in situ polar scattering data (A. Coletti, private communication).

Flo-Master Ink Measurements

Flow master ink, unlike the Mars ink consists entirely of material that is soluble in organic solvents. Like the nigrosine dye the ink forms a true solution. Flo-Master comparisons were made for DT, DR, and FR measurements. The solution measurements exhibited a

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somewhat different wavelength dependence than the diffuse reflec-
tance measurements, possibly due to differences between the Flo-
Master ink as a solution or as solid aerosol particles. B_a values at
633 nm were determined to be 2.7 m^2/g for the DT data (with Nucle-
pore filters as substrates), 1.4 m^2g for the DR data, and 0.6 m^2g
for the FR data. In this case as in the other cases investigated,
use of the FR technique results in significantly lower B_a values
than those measured by the other techniques.

Measurements with this ink were made to investigate the effect
of varying filter media on diffuse transmission measurements. Re-
sults for the Nuclepore filter and the 0.45 μm Millipore filter are
shown in Fig. 7 and Fig. 8. In addition, similar sets of measure-
ments made with a 1.2 μm pore size Millipore filter and with fiber-
glass filters were quite similar to the data shown in Fig.8. No
enhancement of response was seen for any of these filters. These
data, unlike previous data reported for soot aerosol, suggest little
differences among the substrates. In particular, the differences in
pore size for the two Millipore filters appeared to have no signifi-
cant effect on the calculated values. Reasons for these inconsis-
tencies between the data sets are not known at this time. The dif-
ferences may, however, be related to differing penetration depths
into the filters for the different materials.

Additional Comparisons

A further comparison of diffuse transmission and diffuse reflectance techniques for a sooty smoke emission from burning forest fuels is shown in Fig 2. In this figure, the solid line with circles and the solid line with triangles represent B_a values determined for two components(one soluble in methylene chloride and the other non soluble in methylene chloride) of the smoke emissions from flaming combustion; these measurements were made using a combination of DR and solution transmission techniques. The dashed line represents a weighted average of the two components. The x represents a DT measurement of specific absorption in the flaming combustion aerosol. The DT data should lie on the weighted average line; the actual agreement is quite good. In this case, as in the others, the consistency in the different methodologies is excellent.

An additional comparison with volcanic ash also showed a consistency between the DT and the DR techniques. The comparison (for n_2 values) was made with an ash sample from El Chichon volcano. The n_2 values determined for these samples were ~0.0026 for the diffuse transmission technique and ~0.0033 for those measured by diffuse reflectance, numbers that are in agreement within about 25%. There are sample heterogeneities which add an uncertainty in these ash measurements due to sample variability. The uncertainty in these data is estimated to be approximately 20 %, so that there is agreement within the uncertainties of the measurements.

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SUMMARY AND CONCLUSIONS

Several sets of absorption measurements that include comparisons between different techniques for measuring submicron aerosol absorption have been made. These measurements have shown that there is a great deal of consistency among the different techniques when applied to well documented aerosols and that it is possible to provide some definite calibrations of the aerosol measurements in terms of aqueous transmission measurements. The measurements indicate (with the exception of the FR method) that there are no significant systematic errors in the data that are due to differences in techniques as applied in this study. Some specific conclusions follow:

1. It has been shown that the Mars ink is a useful analog of atmospheric soot for absorption measurements and that it can serve as a reproducible, stable aerosol for measurement.

2. The differences in measured B_a values between aqueous and aerosol suspensions have been shown to be important in comparisons of different measurement techniques. Absorption values inferred in an aqueous suspension should be corrected to their values in air before use in aerosol studies.

3. It has been shown that, for our reference Mars ink carbon par-

ticles, the diffuse transmission measurements and the diffuse reflectance measurements using the dilution technique give the B_a value that is expected based on appropriately adjusted direct transmission measurements of the aqueous suspension. This provides a calibration of the diffuse transmission and diffuse reflectance methods in terms of more fundamental measurements.

4. It has been demonstrated that the filter reflectance method systematically underestimates the B_a values of the highly absorbing samples. For the dilution method care must be taken to insure a uniform dilution for the sample.

5. Since the diffuse reflectance technique with dilution gives the expected results, the data indicate that the simple volume mixing rule used to calculate absorption for this method is adequate and that the use of Eq (5) is appropriate.

Table 1

n$_2$ for Mars Ink at 633 nm

Experimental Procedure	B$_a$ (m^2/g)	n$_2$ Best Fit Estimate	Eq (6)	Eq (10)
Diffuse Transmission	2.4	.32		.34
Diffuse Reflectance	3.0		.27	
Aqueous Suspension	2.6	.25		.29

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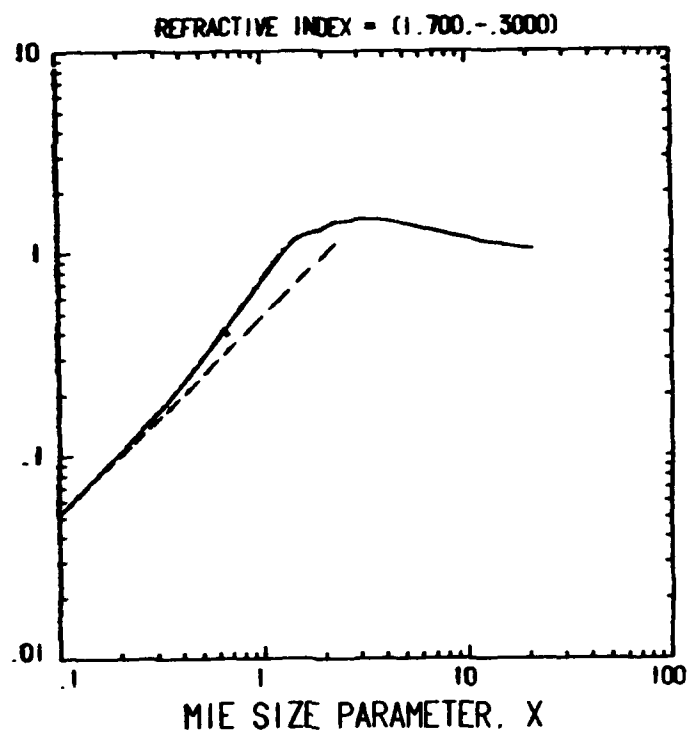
REFRACTIVE INDEX = (1.700.-.3000)

MIE SIZE PARAMETER. X

Fig. 1. Mie absorption efficiency plotted vs the Mie size parameter x. The solid line is the result of exact Mie calculations; the dashed line is the result of applying the approximation in Equation (10).
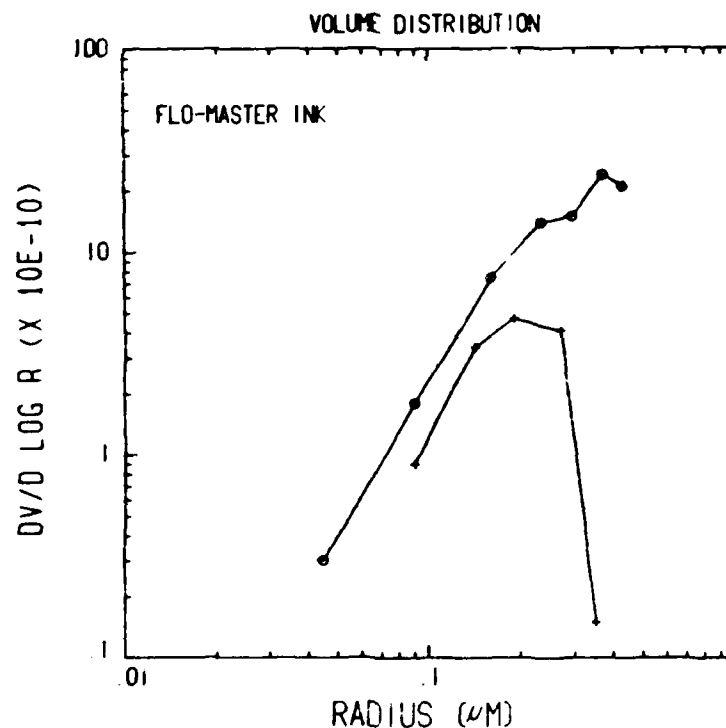
VOLUME DISTRIBUTION

FLO-MASTER INK

DV/D LOG R (X 10E-10)

RADIUS (μM)

Fig. 2. Aerosol mass distribution determined for the Flo-Master ink. The upper curve is a mass distribution determined from scanning electron micrographs; the lower curve from a single particle optical counter. Although the upper curve extends only to 0.5 μm radius, an inspection of the micrographs showed no significant mass in the larger size ranges.

MARS INK (AQUEOUS SUSPENSION)
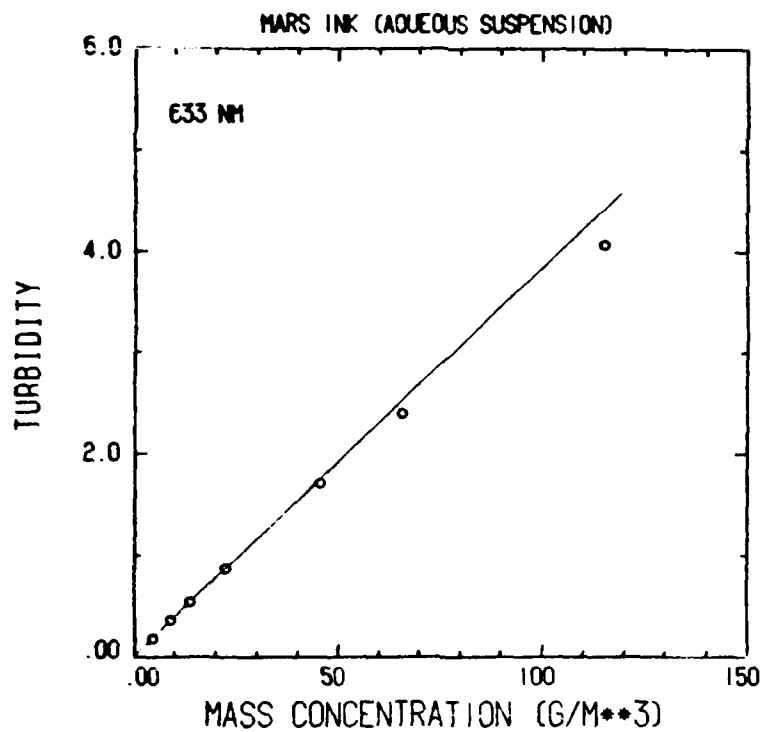
Fig. 3. Measurements of the turbidity of a Mars ink aqueous suspension plotted against mass concentration in a 1 cm path length optical cell.

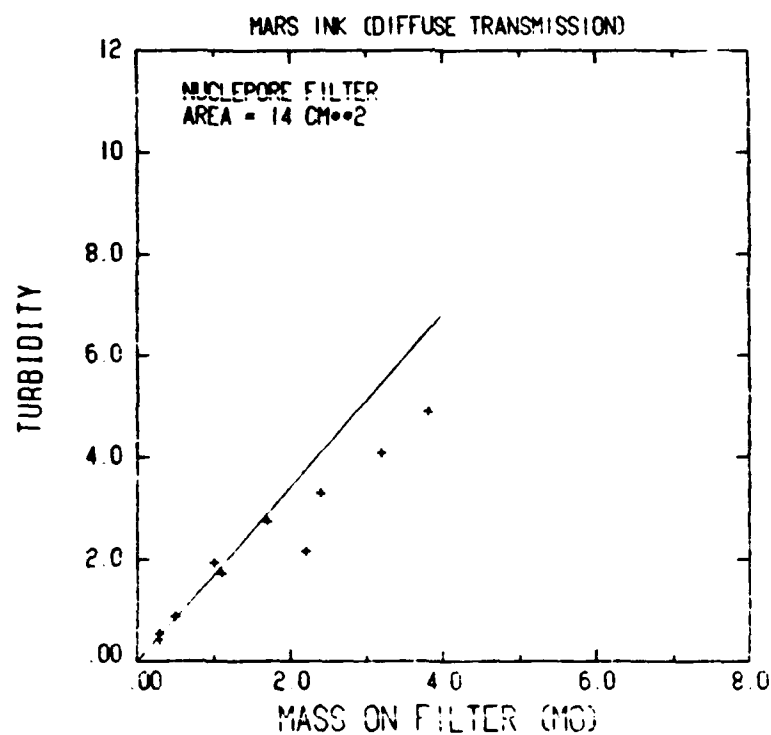MARS INK (DIFFUSE TRANSMISSION)

Fig. 4. Measurements of the turbidity of a Mars ink aerosol plotted against mass concentration on a 14 cm² Nuclepore filter.

MARS INK DATA

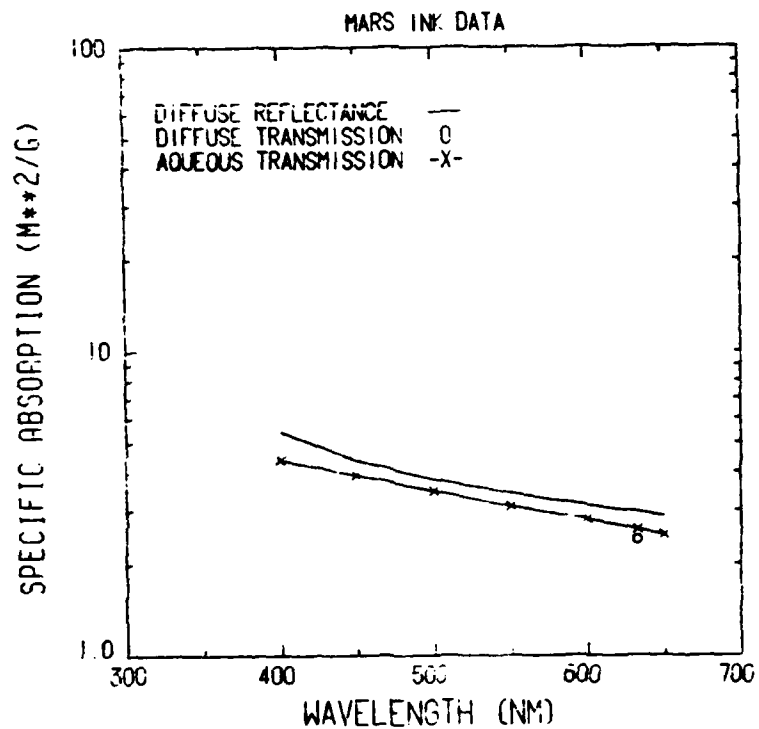Fig. 5. A comparison of B_a values determined for the Mars ink by different measurement techniques. The agreement among the techniques is excellent, both in the absolute values and in the wavelength dependence.
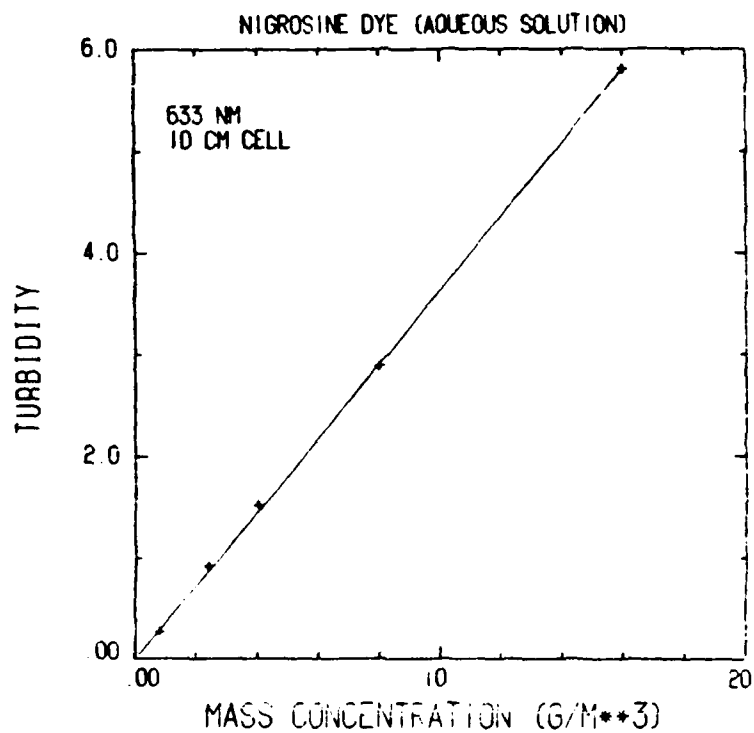
NIGROSINE DYE (AQUEOUS SOLUTION)

Fig. 6. Measurements of the turbidity of a Nigrosine solution plotted against the Nigrosine concentration.

NIGROSINE (DIFFUSE TRANSMISSION)
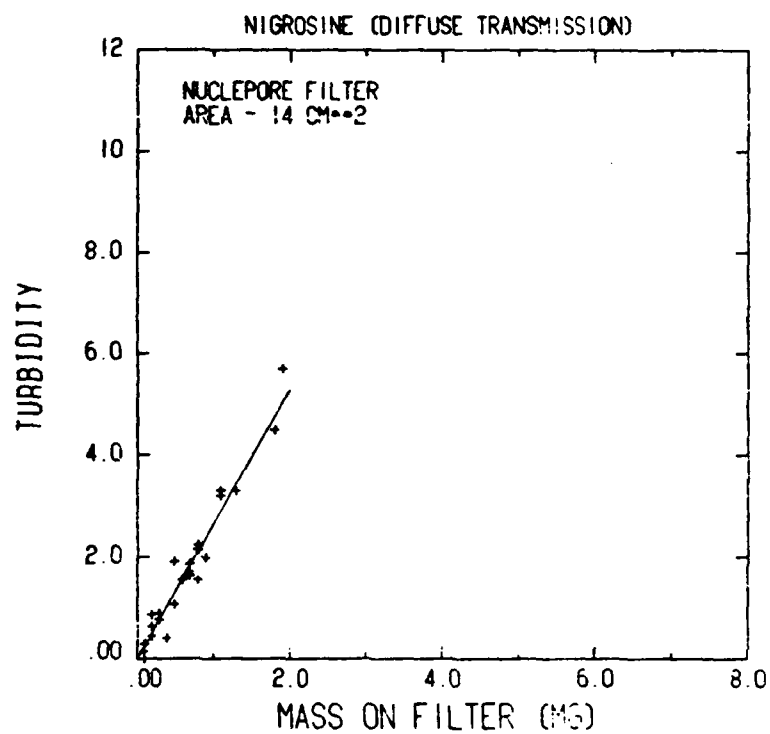
Fig. 7. Measurements of the turbidity of a Nigrosine aerosol collected on a 14 cm² Nuclepore filter vs the mass on the filter.

FLO MASTER INK
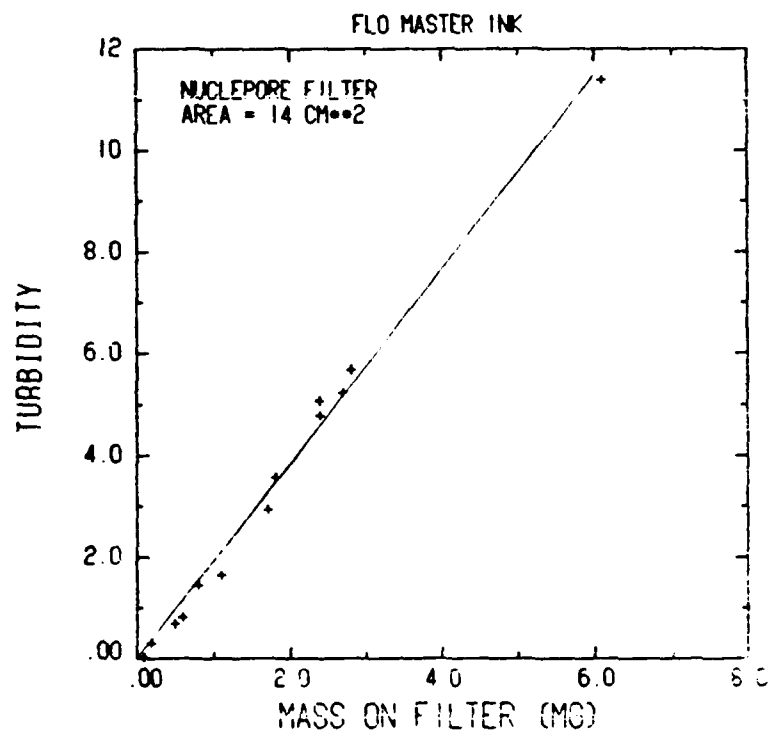

Fig. 8. Measurements of the turbidity of a Flo-Master ink aerosol collected on a 14 cm² Nuclepore filter vs the mass on the filter.
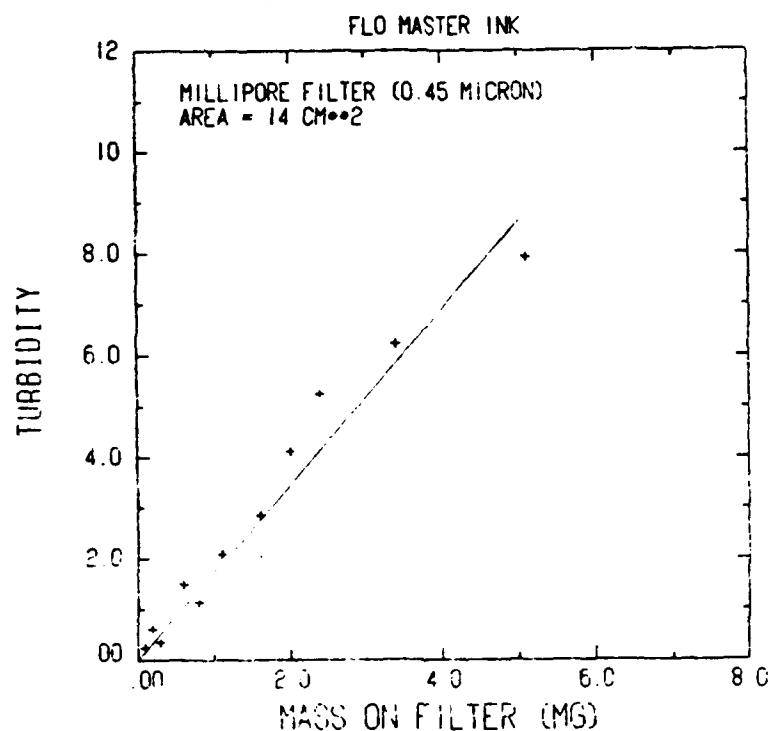
FLO MASTER INK

Fig. 9.   Measurements of the turbidity of a Flo-Master ink aerosol col-
lected on   a 14 cm² Millipore filter vs the mass of aerosol on
the filter.

PINE NEEDLE FIRE-FLAMING PHASE
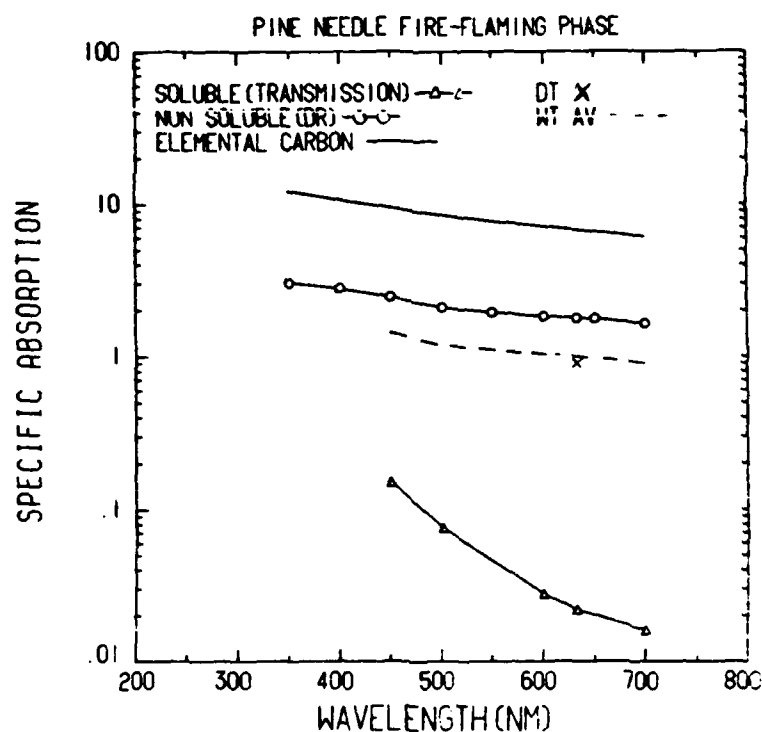

Fig. 10.   Measurements of the absorption properties of smoke emissions
from flaming combustion. The solid line with circles (-o--o-)
represents the wavelength dependent B_a measured for the non-
soluble component determined by diffuse reflectance. The lower
solid line with triangles(-△--△-) represents the B_a measured
for the soluble component by solution transmission. The dashed
line represents a weighted average of the two components.   The
x represents a measurement made by the diffuse transmission
technique for a total filter sample. The upper solid line is
the B_a expected for a pure graphitic carbon aerosol.

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